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PATENT

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For	:	METHOD FOR PLATING AND PLATING SOLUTION THEREFOR
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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03447008.8

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Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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R C van Dijk

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Demande no:

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BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Method for plating and plating solution therefor

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
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PT SE SI SK TR LI

METHOD FOR PLATING AND PLATING SOLUTION THEREFOR.

Technical field of the invention

The invention relates to the field of electroless plating of substrates and in particular to a solution for electroless plating of a substrate as well as a pltaing bath including the solution.

Background of the invention

Use of flexible circuits for electronic assembly is increasing rapidly. Flexible substrates with very fine patterning are necessary in portable electronics (like mobile phones, etc.), advanced chip packages (like CSP's), medical applications (like implants), smart cards, wearable electronics etc.

The most popular base material for high resolution flexible substrates at the moment is polyimide because of its high thermal, mechanical and chemical stability. Onto this base material electrical (interconnection) circuits have to be formed. Adhesion of copper on polyimide is technically not easy and currently 2 types of solutions exist to achieve this goal; 3 layer laminates and 2 layer laminates.

For three layer laminates, a Cu foil, typically 18 or 35μm thick is laminated onto a polyimide base material using an appropriate adhesive. Because of reasons of mechanical stability during handling of the thin Cu foil used in the lamination process, the minimal thickness achievable of the Cu foil is around 12μm in practice. This limits the bendability of the substrate: the thicker the Cu the higher the minimum bending radius of the flexible substrate. The thickness of the Cu layer also determines the minimum pitch features of the flexible substrate circuit (line width – line spacing), since Cu etching will cause underetching and the latter for a depth of the order of the thickness of the Cu layer (thus for a minimal thickness of the Cu foil the pitch is of the order of 40μm). Moreover the adhesive used brings specific problems when mounting components onto the flexible substrate. An example is flip-chip bonding with adhesives, using a thermo-compression step during which the Cu contact pads on the flexible substrate are pressed into the flexible substrate adhesive which melts due to the applied heat (temperature typically 180°C). This reduces the reliability of the product. New adhesives are presently being sought by industry.

At the same time attempts are being made to produce a 2-layer or "adhesiveless" laminate, consisting essentially of Cu and polyimide but the chemical stability of the polyimide means that good adhesion of the Cu to the polyimide is not teasy to achieve.

Electroless Cu deposition processing on flexible substrates is typically based on the following reaction:

$$Cu^{2+} + 2\ HCHO + 4\ OH^- \rightarrow Cu + 2\ HCOO^- + H_2 + 2\ H_2O \text{ (alkaline bath)}$$

This process is catalyzed by either Cu or Pd metallic ions. During pre-treatment of the flexible substrate impurities are removed from the surface and Pd seeds are introduced on the surface of the substrate as a catalyst for the electroless deposition of copper. Further deposition of copper is autocatalytic. In other words the copper acts as a catalyst for further deposition of copper. The interface between the metal and the flexible substrate that is created in this way provides a very low adhesion. To improve the adhesion strength, the surface of the flexible substrate can be roughened before the deposition of electroless copper by means of chemical or plasma treatment (increase of the specific surface of the polymer). An existing solution is to treat the polyimide first in a O_2 plasma, followed by a PVD (physical vapour deposition, i.e. sputtering or evaporation) step, depositing the Cu onto the treated polyimide surface, possibly followed by an electrolytic deposition of Cu onto the PVD layer to increase the total Cu thickness. These treatments have a negative influence on the structural properties of the flexible substrate. This is of even greater importance the thinner the layers.

In G.A. Shafeev, "Light-enhanced electroless Cu deposition on laser-treated polyimide surface", surface treatment of a polyimide surface by laser ablation is performed which results in the formation of a glassy carbon layer at its surface which can mediate electroless Cu deposition.

In other cases the seed layer of copper is not plated by electroless copper but by sputtering some metal onto the flexible substrate surface, because the adhesion strength of the electroless copper onto the flexible substrate is so low that it does not remain on the surface of the flexible substrate .

The complexity of flexible circuits is increasing and double sided circuits, whereby a Cu layer is present on both sides of the polyimide, are advantageous (e.g. used in flexible substrate circuits for CSPs with a flip-chip component on one side of the flexible substrate and solder balls on the other side; this CSP component can then be soldered to a second level substrate, e.g. a PCB). Double sided flexible substrate circuits are typically made starting from a 5-layer laminate (Cu-adhesive-polyimide-adhesive-Cu) or a 3-layer laminate (Cu-polyimide-Cu). The following steps are needed to produce the circuit :

- drilling of the through hole vias;
- via filling by Cu deposition;

- patterning and etching of the Cu on both sides of the substrate.

Lamination of the Cu onto the substrates and via filling are separate steps.

Summary of the invention

A simple and cost-effective method for electroless deposition of a metal, preferably Cu, onto a substrate comprising an insulating surface, e.g. a polymer such as polyimide exposed at a surface thereof is disclosed. A good adhesion of the metal onto the substrate is achieved. The present invention provides a plating solution for electroless deposition of a metal, e.g. Cu, onto a substrate, especially onto a substrate with an insulating surface such as a polymer surface. The polymer may be polyimide. The substrate may have two major surfaces with exposed polymer material or may be composed of a polymer such as polyimide. The present invention provides a solution, in particular for a plating bath for electroless deposition of a metal on a substrate wherein the solution comprises: a source of metal ions; a reducing agent; an additive to adjust the pH of said bath to a predetermined value; and an aromatic sulfonic acid. Typically the metal to be deposited is Cu. The substrate is usually insulating and typically has at least one surface with an exposed polymer such as polyimide. Electroless deposition of the metal onto the substrate, the substrate comprising polyimide exposed at a surface thereof, comprises applying the solution described above. Typical process steps of the method include applying a pre-dip solution, applying a solution with colloidal Pd/Sn catalyst, applying solution comprising an accelerator, and electroless metal Cu deposition by applying the solution described above. Additional steps include cleaning, applying an anti-tarnish solution, and baking.

The present invention allows for producing single–sided or double-sided flexible substrate circuits in a cost effective way. It can combine via filling and deposition of the metal, e.g. Cu, for the interconnection pattern in a single step.

The present invention will now be described with reference to the following drawings.

Brief description of the drawings

Fig. 1 an example of a polyimide.

Fig. 2 an example of an aromatic sulfonic acid.

Description of the preferred embodiments

The present invention will be described with reference to certain embodiments and drawings but these are provided only as examples and the present invention has a wider scope of application.

In a first embodiment of the present invention, a solution, more specifically for a plating bath for electroless deposition of copper on a substrate which comprises an insulating material at its surface is disclosed. This insulating material may be a polymer material and is preferably a polyimide. This polyimide is preferably exposed at a surface of the substrate (example see Fig. 1). The substrate can be an essentially polyimide substrate. The substrate can be flexible. A plating bath according to the invention comprising the solution is preferably an alkaline bath in which the following reaction is possible:

$$CuSO_4 + 2\ HCHO + 4\ NaOH \rightarrow Cu + 2\ HCO_2Na + H_2 + 2\ H_2O + Na_2SO_4$$

Cu itself is also a catalyst for this electroless deposition reaction. The electroless copper deposition bath further comprises an aromatic sulfonic acid (example see Fig. 2).

In a second embodiment of the present invention, a method for electroless deposition of Cu onto a substrate which comprises an insulating material such as a polymer, especially a polyimide is disclosed. The method provides sufficient adhesion of Cu, and uses a sequence of immersions in liquids. It provides a production process for a high performance circuit-on-flex product. Preferably, the substrate is an essentially polyimide substrate. The substrate can be flexible. The resulting products allow fine patterning, small bending radius and a high adhesion of Cu to the flexible substrate. It provides also a smooth surface of the deposited copper. In this method the plating bath according to the first embodiment of the present invention is used as a step in the Cu plating process (as step 5 below) for a surface of a substrate comprising polyimide. The method comprises the following steps (for each of the other steps, similar steps performing the same functions could be applied, or other steps equivalent for somebody ordinary skilled in the art can be used):

Step 1: cleaning the surface:

A 10% $S_2O_8^{2-}/H_2SO_4$ solution is used to remove dirt on the surface of the polymer. This solution is a very strong oxidizing liquid, it is however not able to react with a polymer such as polyimide.

This cleaning step is optional but is preferably included.

Step 2 : Pre-dip solution:

This solution contains Sn^{2+} ions. The goal of immersion in this liquid is to prevent drag-through from the oxidizing agent of the previous step to the following catalyst bath. The following reaction occurs: $Ox + Sn^{2+} \rightarrow Red + Sn^{4+}$

Step 3 : Colloidal Pd/Sn catalyst:

In this liquid Sn^{2+} salt is mixed with Pd^{2+} ions, causing the following reaction:

$$Pd^{2+} + Sn^{2+} \rightarrow Pd + Sn^{4+}$$

The catalyst thus generated is colloidal and adheres to the surface of the polymer.

Step 4: Accelerator:

This step removes the excess Sn from the surface, leaving Pd particles on the surface of the non-conductive material. The Pd particles are a catalyst for the reaction in the following step.

Step 5: Electroless copper:

The copper deposition reaction that occurs is the following:

$$CuSO_4 + 2\ HCHO + 4\ NaOH \rightarrow Cu + 2\ HCO_2Na + H_2 + 2\ H_2O + Na_2SO_4$$

Cu itself is also a catalyst for this electroless deposition reaction. Further deposition of copper is possible in this way. The electroless copper deposition bath further comprises at least one aromatic sulfonic acid in order to promote a high adhesion strength between Cu and polymer surface.

Step 6 : Anti-Tarnish:

This solution contains components that adsorb on the surface and prevent oxidation of the copper.

Step 7: Baking step:

The baking step includes heating to a suitable temperature to remove excess water and hydrogen from the surface of the copper. The step will typically invlove

temperatures greater than 100°C at atmospheric pressure, e.g. between 150°C and 200°C.

In a specific embodiment the previous steps applied on a polyimide substrate can be:

Step 1: etching liquid at 20°C.
Step 2: Shipley Circuposit Pre-dip 3340 at room temperature
Step 3: Shipley Circuposit Catalyst 3344 at 30°C.
Step 4: Shipley Circuposit Accelerator 19H at room temperature
Step 5: Shipley Circuposit Electroless Cu + additives, comprising an aromatic sulfonic acid or acids, at 27°C.
Step 6: Shipley Anti Tarnish 7130 at room temperature for 3 minutes
Step 7: Baking at 150°C for 60 minutes.

Deposition rates of typically 0.5 to 1 μm per minute have been measured. Any thickness of Cu layer can be achieved and thus theoretically every pitch, e.g. for connection wiring layers. For conductivity reasons the thickness is preferably higher then 2μm. Even more preferably the thickness is higher then 3μm. The latter case corresponds to a pitch of the order of 10μm.

The surface of the resulting Cu layer is essentially smooth and does not have to be smoothed in an extra step, before typical further use.

The resulting adhesion strength is high. The Scotch tape test has been performed with success and is defined as follows: apply a Pressure-sensitive tape to an area of the coating which is sometimes cross-hatched with scratched lines. Adhesion is considered to be adequate if coating is not pulled off by the tape when it is removed.

Without being limited by theory, it is believed that the high adhesion strength between the Cu and the polyimide substrate resulting from use of the plating bath according to the present invention is caused by chemisorption and thus chemical anchoring, mediated by the presence of at least one aromatic sulfonic acid in the plating bath. By introducing a chemical bond between both layers (polyimide and Cu) it is possible to improve the adhesion strength significantly, because chemically bonded interfaces have much stronger interactions between both of the different materials then interfaces that are simply bound by adsorption. Furthermore, the presence of one or more aromatic sulfonic acids also facilitates the formation of

hydrogen bubbles, which are formed during the electroless deposition process and can burden the deposition of a homogeneous copper layer.

The surface of the polyimide does not need to be roughened or plasma treated before or during the deposition process.

It has been shown that further steps as patterning and etching are easily possible.

The method according to the second embodiment of the present invention requires only chemicals that are relatively cheap. It has reel-to-reel capability. Deposition of thin Cu layers, and thus high density and highly bendable flexible substrate is made possible by the present invention.

In an aspect of the second embodiment of the present invention the method can be used for production of double sided flexible substrate circuits by deposition of the Cu for filling of the vias (or through holes) and for realizing the interconnections (after patterning and etching the resulting copper layer) in a single step. Since the electroless process is a catalytic chemical process, uniform plating is possible in via's, holes and the surface of the flexible substrate simultaneously.

A Double-sided flexible substrate production process can comprise the following steps

- Start from a single layer polyimide material or a material with polyimide exposed on two major surfaces
- Drill (e.g. by laser) via's (through holes) in the substrate if required
- Electroless deposition of Cu on both sides of the flexible substrate and in the holes according to second embodiment of the present invention.
- Patterning and etching the Cu on both sides of the flexible substrate

In an aspect of the second embodiment of the present invention, the plating bath can be applied locally. This local application can comprise a masking step that divides the surface area of the substrate into active and non-active zones, for instance in large sub-areas of the substrate or in other patterns on the substrate, such that a good adhesion can be achieved selectively.

Instead of copper, also other metals such as e.g. Au, Ca, Al can be deposited by the method according to the second embodiment of the present invention by providing suitable source of metal ions in the plating solution.

While the invention has been shown and described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention.

Claims

1. A solution, in particular for a plating bath for electroless deposition of a metal on a substrate wherein the solution comprises:
    - a source of metal ions;
    - a reducing agent;
    - an additive to adjust the pH of said bath to a predetermined value; and
    - an aromatic sulfonic acid.
2. The solution according to claim 1, wherein the metal is Cu.
3. A method for electroless deposition of a metal on a substrate, the substrate comprising polyimide exposed at a surface thereof, comprising applying the solution according to claim 1 to 2.
4. A method for electroless deposition of a metal onto a substrate, said substrate comprising polyimide exposed at a surface thereof, comprising:
    - applying a pre-dip solution
    - applying a solution with colloidal Pd/Sn catalyst
    - applying solution comprising an accelerator, and
    - electroless Cu deposition by applying the solution according to claim 1 or 2.
5. A method according to claim 4, further comprising a preliminary step of cleaning a surface of the substrate.
6. A method according to claim 4 or 5, further comprising:
    - Applying an anti-tarnish solution, and
    - Baking.
7. A method according to any of claims 3 to 6, wherein the substrate is flexible.
8. A method according to any of claims 3 to 7, wherein the surface consists essentially of polyimide.
9. A method according to any of claims 3 to 8, wherein the substrate is a polyimide substrate.
10. A method according to any of claims 3 to 9, wherein the substrate comprises through holes or vias.

Abstract

A solution is described, in particular for a plating bath for electroless deposition of a metal on a substrate. The solution comprises: a source of metal ions; a reducing agent; an additive to adjust the pH of said bath to a predetermined value; and an aromatic sulfonic acid. The solution is used in a method for electroless deposition of a metal on a substrate wherein the substrate preferably comprises polyimide exposed at a surface thereof. The method may comprise: applying a pre-dip solution, applying a solution with colloidal Pd/Sn catalyst, applying solution comprising an accelerator, and electroless Cu deposition by applying the solution described above. Further steps comprise applying an anti-tarnish solution, and baking.

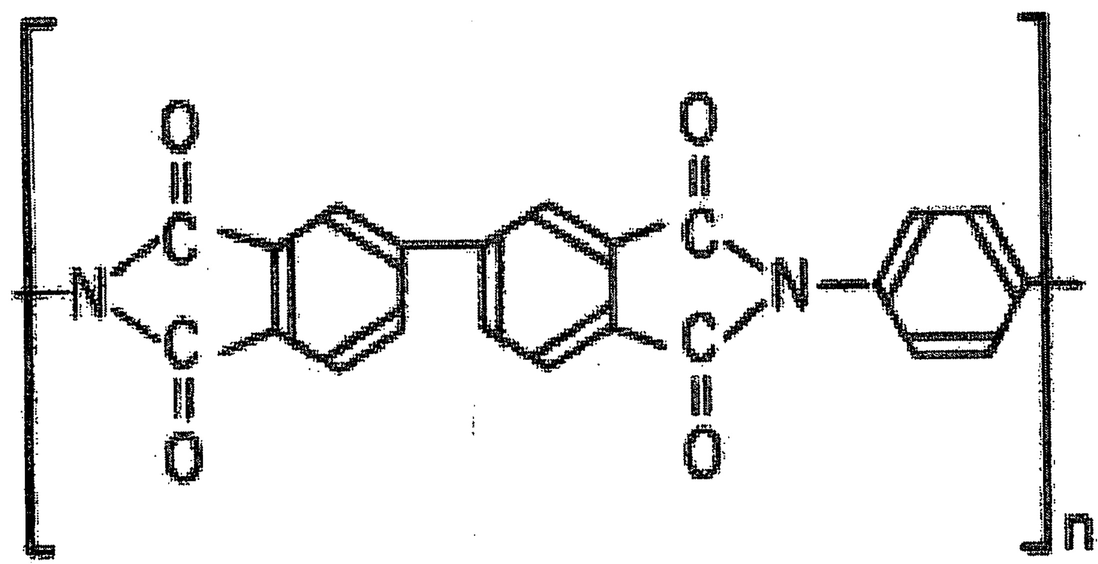

Fig. 1

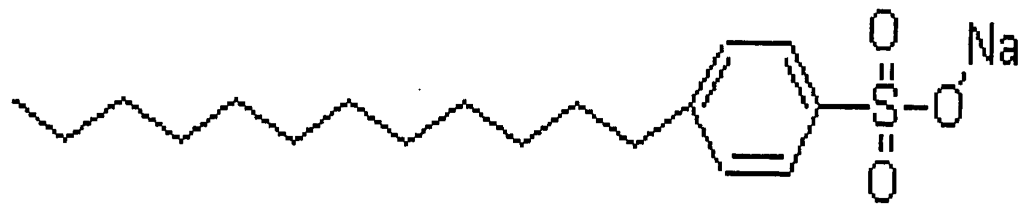

Fig. 2